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# OXIDE ZINC CERAMICS FOR VARISTORS (A Review)

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Ceramics based on zinc oxide used in the production of varistors are considered. The most probable mechanism of the non-ohmic behavior of the material with various dopants under an electric field effect is discussed.

Nonlinear elements, i.e., instruments whose service property consists in a essentially nonlinear functional dependence are extensively used in electrical engineering and electronics. The nonlinear volt-ampere characteristic (VAC) of these instruments makes it possible to solve a number of technical problems: to control and stabilize the operation of individual units of electronic equipment, to improve noise stability of automated amplification control systems, etc. [1]

Nonlinear elements include ceramic varistors which can be molded to the desired shapes and sizes, which allows for their versatile application. It is quite likely that the use of varistors will expand as their technology improves.

The varistors are semiconductor resistors with a nonlinear VAC. They have high ohmic resistance with low voltage, and, vice versa, low resistance with high voltage, i.e., high electric conductance (Fig. 1). The voltage level at which the current passing through the varistor sharply increases is called the break-down voltage, or the threshold voltage $U_{br}$.

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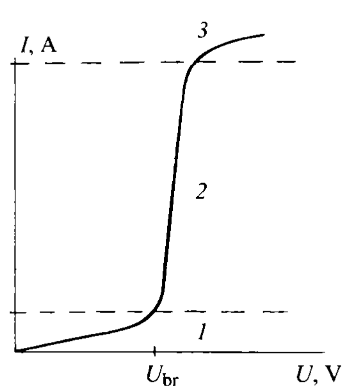


**Fig. 1.** Typical volt-ampere characteristic of a varistor: *1*) pre-breakdown; *2*) breakdown; *3*) inversion.

The electric properties of these elements cannot be described by the Ohm law and are called non-ohmic. The volt-ampere curves are approximated by the equation

$$I = BU^{\beta},$$

where $I$ is the current, A; $U$ is the voltage, V; $B$ and $\beta$ are constants.

The constant $\beta$ characterizes the VAC nonlinearity and is called the nonlinearity coefficient. For varistors, coefficient $\beta$ is significantly higher than 1.

The weak current region is called the pre-breakdown region *1* and physically it corresponds to the very weak currents passing through the varistor at a voltage level below the breakdown voltage. The current within the breakdown region *2* is extremely nonlinear and varies significantly with slight variations in the applied field. The region of very heavy currents *3* is denoted as the inversion region and is determined by the consecutive resistance of ZnO grains [2].

It was found [3] that the region of non-ohmic behavior of the varistor becomes narrower with an increase in the temperature, and nonlinearity coefficient $\beta$ at the temperature of 650°C decreases to zero due to the temperature dependence between current and voltage.

The first varistors were made of silicon carbide. Owing to the various shortcomings of these varistors, contemporary elements are made of zinc oxide, which possesses semiconductor properties. According to its electric conductance, zinc oxide belongs to the *n*-type with a donor density of $10^{17} - 10^{19}$ cm$^{-3}$ and specific resistance of 1 Ohm · cm. To dope the material and impart varistor properties to it, oxides of Bi, Co, Pr, Mn, Cr, Sb, Ti and others are introduced.

There are numerous theoretical models of conductance in non-ohmic ceramics of zinc oxides [2, 4 – 7], but they are virtually all based on the conventional conjectures and assumptions.



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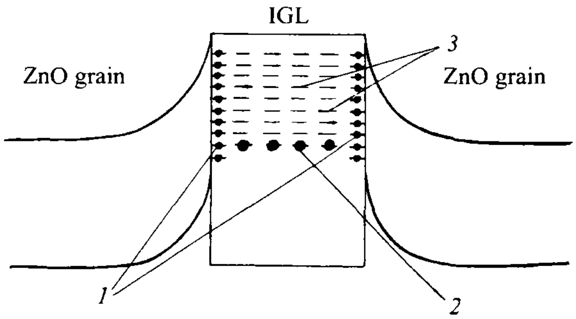


**Fig. 2.** Semiconductor – insulator – semiconductor structure: intergranular layer and the surrounding Schottky barriers formed on the surface of ZnO grains: *1* ) surface states; *2* ) a trap; *3* ) vacant levels.

The non-ohmic properties of ZnO ceramics are determined by the presence of intergranular layers (IGL) with high resistance positioned between ZnO grains having low resistance and Schottky barriers formed on the grain surfaces (Fig. 2). The Schottky barrier arises due to the surface state caused by the dopants. The thickness of an IGL is no more than 500 Å, and its has a lot of traps.

The electrons which, due to thermal ionic emission, penetrate from the ZnO grain conductance zone along the direct Schottky barrier into the IGL, move within the IGL by means of multitunneling via traps or impurity levels and reach the surface states on the opposite side of the IGL. Then they tunnel through the inverse Schottky barrier from the surface states to the conduction zone according to the electric field emission mechanism with a voltage level exceeding the breakdown voltage, and a thermal ionic emission mechanism with voltage below the breakdown level.

The varistors based on zinc oxide usually consist of ZnO (85 – 99 mole %), and the rest (1 – 15%) are constituted by various dopants. Each doping additive has its role in the formation of the material structure and formation of varistor properties.

The first group includes doping oxides which produce a liquid phase upon sintering:

$Bi_2O_3$ and $Co_2O_3$ support phase stability;

$MnO_2$ and $CrO_3$ provide for material stability as well;

NiO takes part in the formation of a microstructure that withstands a fixed and variable voltage load.

$B_2O_3$ and $SnO_2$ also belong to this group.

The second group includes growth modifiers for ZnO grains:

$Sb_2O_3$ , $SiO_2$ retard the growth of crystals;

$TiO_2$ , on the contrary, accelerates growth of grains.

It is established that titanium ions in sintering are distributed over the liquid phase of $Bi_2O_3$ and intensify the chemical activity with respect to ZnO particles [8].

The third group includes the dopants which affect the electric properties of the varistors.

Aluminum oxide in a vitreous matrix is positioned around the ZnO grains. In extremely low quantities

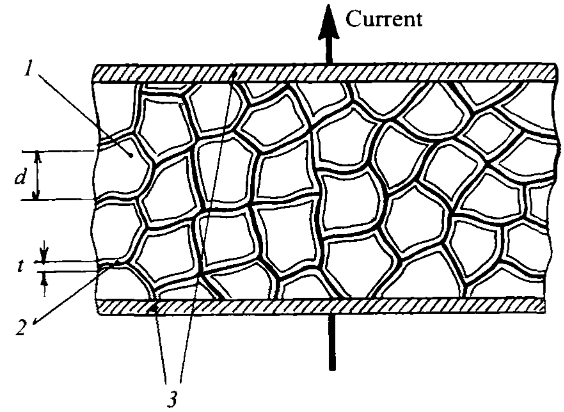


**Fig. 3.** Microstructure of varistor ceramics: *d* ) ZnO grain size; *t* ) width of "depletion" area; *1* ) the grain; *2* ) the boundary; *3* ) the electrodes.

(~ $10^{-4}$ %), $Al_2O_3$ increases the conductivity of ZnO. With a high content of $Al_2O_3$ , it diffuses to the boundary areas of the grains and can produce heavy leakage currents and a decrease in the intergrain activity (Great Britain patent GB 2242065A).

It was found in [9] that $Al^{3+}$ ions are the carrier donors in a ZnO semiconductor, and with an increase in their concentration, the leakage current in the region before breakdown increases (the specific resistance decreases), and the dynamic resistance in the inversion region decreases.

$Ga^{3+}$ ions produce a similar effect.

$Li^{+}$ ions in ZnO act as acceptors and have the opposite effect on ceramic properties.

Varistors can contain Mn, Co, and Cr in the form of differently charged cations, such as $Mn^{2+}$ and $Mn^{3+}$, $Co^{2+}$ and $Co^{3+}$, $Cr^{2+}$ and $Cr^{3+}$, which can probably control the concentration of the oxygen vacancies in the structure. These ions can also act as acceptors for the electrons which are liberated when vacancies are formed by oxygen anions [10].

The divalent manganese ions increase the Schottky barrier at the dividing boundary and improve the non-ohmic properties of ZnO ceramics [7].

The role and significance of MgO in varistor ceramics has not yet been fully studied, but it is a standard component.

The behavior of a varistor is determined by its microstructure. It is shown schematically in Fig. 3. A varistor consists of conducting zinc oxide grains of size *d* surrounded by a thin (several nanometers) layer [4, 6], which is enriched with dopant cations and divides the grains. The typical grain size is ~ 10 μm, and their specific resistance is no more than 1 Ω · cm. On the surface of each grain, an insulating boundary layer ~ 100 nm thick deprived of oxygen ions is formed. These "depletion" layers are totally inside the grain and in fact they control the varistor's behavior.

The breakdown voltage per barrier between grains is 3.2 V, considering that the current always takes the path with the least number of the barriers between the electrodes.

It is evident from Fig. 3 that the electric characteristics of the varistor relate to the material mass, i.e., the varistor action is distributed between different boundaries of ZnO grains. Hence, in order to obtain a device with a prescribed breakdown voltage, it should contain a corresponding number of grains consecutively connected between the electrodes. In order to obtain the desired breakdown voltage, it is possible to modify the grain size by increasing or decreasing the number of barriers while the element thickness remains constant, or to modify the varistor thickness while maintaining a permanent size of the grains.

It is necessary to stress that the insulating barrier of thickness $t$ is not a separate phase but adjacent "depletion" layers at the boundaries between ZnO grains [5, 11, 12].

The electric properties of varistors are determined only by the behavior of the grain – grain individual junctions. The proper varistor voltage depends on the number of grain boundaries located between the electrodes. However, the homogeneity of the microstructure as well is a very significant parameter of the device, since conduction between the electrodes is implemented by numerous parallel paths. A slight disturbance, for examples, in the number of grain boundaries along different current flow directions, which may be caused by suboptimum manufacturing and sintering procedures, can produce significant current variations at different sites of the varistor disk surface. Such behavior can have a profound effect on the varistor parameters, especially at high current values, even in the case when the electric parameters of the individual barriers are optimum [3].

The conduction inside the grains is ohmic, which adds to the breakdown voltage value

$$U_g = I\rho_g,$$

where $\rho_g$ is the specific conductivity of the grain.

This voltage produces an inflection visible in Fig. 1 at high current values and is the limiting feature in operation of metal oxide varistors used to suppress overvoltage.

The level of voltage protection of a circuit is not the breakdown voltage but a higher value, due to a voltage drop inside the grains.

While pure ZnO is an insulating semiconductor with a forbidden band width of ~ 0.5 eV, ZnO with dopants has significant conductance. The conductance arises due to the low levels of the donors in ZnO related to the oxygen vacancies which are formed in sintering at the temperature of about 1200°C [13]. Such dopants as Al or Li can to a certain extent control the specific conductance of the grains.

Thus, zinc oxide varistors have significantly higher nonlinearity of VAC, as compared to silicon carbides. The electrical characteristics of such a varistor depend on the structure of its material.

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